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(21) International Application Number: PCT/US99/24275 (22) International Filing Date: 19 October 1999 (19.10.1999) (30) Priority Data: 09/174,891 19 October 1998 (19.10.1998) US (60) Parent Application or Grant HUNTSMAN PETROCHEMICAL CORPORATION [?]; (). ANANTANENI, Prakasa, Rao [?]; (). O'KEEFE, Robert, M.; ().	Published	
(54) Title: ALKYLATION OF BENZENE TO FORM LINEAR ALKYL BENZENES USING FLUORINE-CONTAINING MORDENITES (54) Titre: ALKYLATION DU BENZENE POUR LA FABRICATION D'ALKYLBENZENES LINEAIRES AVEC UTILISATION DE MORDENITES FLUOREES		
(57) Abstract <p>This invention is directed to a fluorine-containing mordenite catalyst and use thereof in the manufacture of linear alkylbenzene (LAB) by alkylation of benzene with an olefin. The olefin may have from about 10 to 14 carbons. The fluorine-containing mordenite is prepared typically by treatment with an aqueous hydrogen fluoride solution. The benzene alkylation may be conducted using reactive distillation. This invention is also directed to a process for production of LAB having a high 2-phenyl isomer content by use of the fluorine-containing mordenite in conjunction with a conventional solid LAB alkylation catalyst. The two catalysts may be used in a mixed catalyst bed or may be packed in series, with the relative proportions being adjusted to provide a desired 2-phenyl isomer content in the final product.</p> (57) Abrégé <p>La présente invention concerne un catalyseur à mordenite renfermant du fluor et son emploi dans la fabrication d'alkylbenzènes linéaires (LAB) par alkylation du benzène avec une paraffine. Cette paraffine peut comporter de 10 à 14 atomes de carbone. La mordenite fluorée s'obtient généralement par traitement avec une solution aqueuse de fluorure d'hydrogène. L'alkylation du benzène peut se faire par distillation avec réaction. Cette invention concerne également la production de LAB à teneur élevée en 2-phényle isomère au moyen d'une mordenite fluorée avec un catalyseur d'alkylation LAB solide classique. Les deux catalyseurs peuvent être utilisés dans un lit catalytique mélangé ou bien être empilés en série, avec ajustement des proportions relatives en vue de l'obtention de la teneur requise en 2-phényle isomère pour le produit final.</p>		

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(21) International Application Number: PCT/US99/24275 (22) International Filing Date: 19 October 1999 (19.10.99) (30) Priority Data: 09/174,891 19 October 1998 (19.10.98) US (71) Applicant: HUNTSMAN PETROCHEMICAL CORPORATION (US/US); Russell R. Stolle, 7114 North Lamar Boulevard, Austin, TX 78746 (US). (72) Inventor: ANANTANENI, Prakasa, Rao, 13019 Partridge Bend Drive, Austin, TX 78729 (US). (74) Agent: O'KEEFE, Robert, M.; O'Keefe, Egan & Peterman, LLP, 1101 Capital of Texas Highway South, Building C, Suite 200, Austin, TX 78746 (US).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: ALKYLATION OF BENZENE TO FORM LINEAR ALKYL BENZENES USING FLUORINE-CONTAINING MORDENITES		
(57) Abstract <p>This invention is directed to a fluorine-containing mordenite catalyst and use thereof in the manufacture of linear alkylbenzene (LAB) by alkylation of benzene with an olefin. The olefin may have from about 10 to 14 carbons. The fluorine-containing mordenite is prepared typically by treatment with an aqueous hydrogen fluoride solution. The benzene alkylation may be conducted using reactive distillation. This invention is also directed to a process for production of LAB having a high 2-phenyl isomer content by use of the fluorine-containing mordenite in conjunction with a conventional solid LAB alkylation catalyst. The two catalysts may be used in a mixed catalyst bed or may be packed in series, with the relative proportions being adjusted to provide a desired 2-phenyl isomer content in the final product.</p>		

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1 ALKYLATION OF BENZENE TO FORM LINEAR ALKYL BENZENES
2 USING FLUORINE-CONTAINING MORDENITES
3

4 By:
5

6 Prakasa Rao Anantaneni
7

8 BACKGROUND OF THE INVENTION
9

10 This invention generally relates to the alkylation of benzene with olefins using
11 mordenite catalysts.
12

13 Linear alkylbenzenes (LAB's) having long chains (typically 10-14 carbons) are
14 commonly used, commercial products. LAB's are commonly sulfonated to thereby produce
15 surfactants.
16

17 Typically, LAB's are manufactured commercially using classic Friedel-Crafts chemistry,
18 employing catalysts such as aluminum chloride, or using strong acid catalysts such as hydrogen
19 fluoride, for example, to alkylate benzene with olefins. While such methods produce high
20 conversions, the selectivity to the 2-phenyl isomer is low, generally being about 30% or less.
21 LAB's with a high percentage of the 2-phenyl isomer are highly desired because such
22 compounds when sulfonated have long "tails" which provide enhanced solubility and detergent
23 properties.
24
25

SUMMARY OF THE INVENTION

It has now been recognized that a need exists for a method of LAB production having high substrate olefin conversion, high selectivity to 2-phenyl isomer LAB, and employing a catalyst having long lifetimes and easy handling. This invention provides a solution to one or more of the problems and disadvantages described above.

The mordenite catalyst of this invention may be mixed with a different catalyst that does not afford high 2-phenyl isomer LAB production. The amounts of each catalyst can thus be adjusted to provide the desired levels of 2-phenyl isomer LAB in the product stream. In this way, LAB may be produced having a higher 2-phenyl isomer content than would be produced using the non-mordenite catalyst of this invention.

In one broad respect, this invention is a process for the production of linear alkylbenzenes, comprising:

contacting benzene and an olefin having about 8 to about 30 carbons in the presence of a mixed catalyst bed to form linear alkylbenzenes, wherein the mixed catalyst bed comprises fluorine-containing mordenite and a second, solid linear alkylbenzene alkylation catalyst, wherein the second alkylation catalyst has a selectivity to the 2-phenyl isomer of the linear alkylbenzenes less than the selectivity of the fluorine-containing mordenite.

In another broad respect, this invention is a process for the production of linear alkylbenzenes, comprising:

dehydrogenating a paraffin to form an olefin;

sending a feed stream of benzene and the olefin through a conduit to a linear alkylbenzenes alkylation reactor containing a fluorine-containing mordenite and a second alkylation catalyst, wherein the second alkylation catalyst has a selectivity to the 2-phenyl isomer of the linear alkylbenzenes less than the selectivity of the fluorine-containing mordenite;

reacting the benzene and olefin in the reactor to form a crude linear alkylbenzenes stream;

1 distilling the crude linear alkylbenzenes stream in a first distillation column to
2 separate benzene that did not react and to form a benzene-free linear alkylbenzenes stream;
3 distilling the benzene-free linear alkylbenzenes stream in a second distillation column
4 to separate any paraffin present and to form a paraffin-free linear alkylbenzenes stream;
5 distilling the paraffin-free linear alkylbenzene stream in a third distillation column to
6 provide an overhead of a purified linear alkylbenzene stream and removing a bottoms stream
7 containing heavies.

8
9 This invention, in another broad respect, is a process useful for the production of
10 monoalkylated benzene, comprising contacting benzene with an olefin containing from about 8
11 to about 30 carbons in the presence of fluorine-containing mordenite under conditions such that
12 linear monoalkylated benzene is formed.

13
14 In a second broad respect, this invention is a process useful for the production of
15 monoalkylated benzene, comprising introducing a feed comprising olefin having about 8 to
16 about 30 carbons and benzene into a fluorine-containing mordenite catalyst bed under
17 conditions such that monoalkylated benzene is produced, allowing benzene, olefin, and
18 monoalkylated benzene to descend (fall) into a reboiler from the catalyst bed, removing
19 monoalkylated benzene from the reboiler, and heating the contents of the reboiler such that
20 benzene refluxes to further contact the fluorine-containing mordenite.

21
22 In another broad aspect, this invention relates to mordenite useful for alkylating benzene
23 with olefin having a silica to alumina molar ratio of about 10:1 to about 100:1; wherein the
24 mordenite has been treated with an aqueous hydrogen fluoride solution such that the mordenite
25 contains from about 0.1 to about 4 percent fluorine by weight.

26
27 In another broad respect, this invention is a method useful for the preparation of
28 fluorine-containing mordenite, comprising contacting a mordenite having a silica to alumina
29 molar ratio in a range from about 10:1 to about 100:1 with an aqueous hydrogen fluoride
30 solution having a concentration of hydrogen fluoride in the range of from about 0.1 to about 10

1 percent by weight such that the mordenite containing fluorine is produced, collecting the
2 fluorine-containing mordenite by filtration, and drying.

3
4 The fluorine treated mordenite catalyst advantageously produces high selectivities to the
5 2-phenyl isomer in the preparation of LAB, generally producing selectivities of about 70
6 percent or more. Also, the fluorine treated mordenite enjoys a long lifetime, preferably
7 experiencing only a 25 percent or less decrease in activity after 400 hours on stream. A process
8 operated in accordance with the apparatus depicted in FIGS. 1 and 2 has the advantage that
9 rising benzene from the reboiler continuously cleans the catalyst to thereby increase lifetime of
10 the catalyst. In addition, this invention advantageously produces only low amounts of
11 dialkylated benzene, which is not particularly as useful for detergent manufacture, as well as
12 only low amounts of tetralin derivatives.

13
14 Certain terms and phrases have the following meanings as used herein.

15
16 "Meq/g" means milliequivalents of titratable acid per gram of catalyst, which is a unit
17 used to describe acidity of the catalysts. Acidity is generally determined by titration with a
18 base, as by adding excessive base, such as sodium hydroxide, to the catalyst and then back
19 titrating the catalyst.

20
21 "Conv." and "Conversion" mean the mole percentage of a given reactant converted to
22 product. Generally, olefin conversion is about 95 percent or more in the practice of this
23 invention.

24
25 "Sel." and "Selectivity" mean the mole percentage of a particular component in the
26 product. Generally, selectivity to the 2-phenyl isomer is about 70 or more in the practice of this
27 invention.

28
29 The mordenite catalyst of the present invention is useful as a catalyst in the production
30 of LAB's in accordance with the process of manufacturing LAB's of this invention. LAB is
31 useful as starting material to produce sulfonated LAB, which itself is useful as a surfactant.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a representation of a first continuous reactive distillation column employed in the practice of this invention.

FIG. 2 shows a representation of a second continuous reactive distillation column employed in the practice of this invention.

FIG. 3 shows a representative process scheme for one embodiment of this invention where a fluorine-containing mordenite is employed with a second, solid catalyst to achieve variable 2-phenyl isomer content depending on the relative proportions of the two catalysts.

DETAILED DESCRIPTION OF THE INVENTION*Catalyst Preparation and Properties*

The catalyst of this invention is a fluorine-containing mordenite. Mordenite is a type of zeolite. The catalyst of this invention is prepared from hydrogen mordenite (typically having 0.1 percent or less of sodium) having a silica-alumina molar ratio of from about 10:1 to about 100:1. More typically, the starting mordenite has a silica/alumina molar ratio of from about 10:1 to about 50:1. The starting hydrogen mordenite, which is commonly available commercially, is treated with an aqueous solution of hydrogen fluoride ("HF") to produce the active, long-life and highly selective catalyst of the invention. In the course of such HF treatment, as well as during subsequent calcination of said HF-treated mordenite, the silica/alumina molar ratio typically increases. The finished catalysts of this invention show a fluorine content of from about 0.1 to about 4 percent by weight, more typically about 1 percent.

While not wishing to be bound by theory, it is believed that the HF reacts with sites where -Si-O-Al- linkages occur such that the linkage is broken with fluorine becoming bonded to the Al such that -Si-OH and F-Al- groups form. This is believed to decrease the total Bronsted acid sites and increase the strength of the remaining acid sites in the mordenite and is

1 believed to stabilize the acidity of the mordenite such that the mechanisms which degrade
2 performance during LAB production, such as coke build-up, are retarded.

3
4 The aqueous solution used to treat the mordenite may contain a range of HF
5 concentrations. Generally, the HF concentration is a minimum of about 0.1 percent by weight.
6 Below such minimum concentration, the effect of the fluorine treatment significantly decreases,
7 resulting in the undesirable need for repeated treatments. Generally, the HF concentration on
8 the upper end is about 10 percent by weight or less. Above a concentration of about 10 percent
9 by weight, the HF is so concentrated that it is difficult to prevent HF from destroying the
10 crystallinity of the mordenite, thereby detrimentally affecting its efficacy as a catalyst for LAB
11 production.

12
13 The aqueous HF solution may be prepared by diluting commercially available 48% HF
14 solutions to the desired concentration. Alternatively, HF can be sparged into water to provide
15 an aqueous HF solution.

16
17 Typically, the treatment is carried out by adding mordenite powder or pellets to a stirred
18 aqueous HF solution at a temperature of from about 0°C to about 50°C. The stirring and
19 contacting is continued for a time sufficient to achieve the desired level of fluorine in the
20 mordenite. This time may vary depending on factors such as HF concentration, amount of HF
21 solution relative to the amount of mordenite being treated, speed of agitation is employed, and
22 temperature. After treatment, the mordenite can be recovered by filtration, and then dried. It is
23 also possible to impregnate the mordenite to incipient wetness with a given HF solution, as well
24 as to treat the mordenite with gaseous hydrogen fluoride. Preferably said fluoride-treated
25 mordenite would be calcined in air prior to use in alkylation service. The preferred calcination
26 temperature would be in the range from about 400°C to about 600°C. Alternative mordenite
27 fluorinating agents to hydrofluoric acid and hydrogen fluoride include ammonium fluoride,
28 fluorided silicon compounds and fluorided hydrocarbons.

29
30 The HF-treated mordenite of this invention generally has about 0.1 percent by weight or
31 more of fluorine based on the total weight of the mordenite. Typically, the fluorine-containing

1 mordenite contains about 4 percent by weight or less fluorine. The fluorine-containing
2 mordenite most typically contains about 1 percent by weight of fluorine.

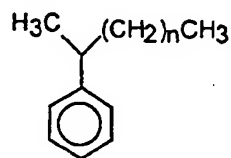
3
4 The mordenite can be used in the practice of this invention as a powder, in pellet
5 form, as granules, or as extrudates. The mordenite can be formed into pellets or extrudates
6 using binders well known to those of skill in the art, such as alumina, silica or mixtures
7 thereof.

8
9 *Reactants for LAB Production*

10
11 In the practice of this invention, benzene is alkylated with olefin to form LAB. These
12 reactants can be handled and purified as is generally performed by those of skill in the art. In
13 this regard, it is preferred that the reactants are water and alcohol free. The olefins employed in
14 the practice of this invention have from about 8 to about 30 carbons, preferably from about 10
15 to about 14 carbons, such as is available commercially or produced as dehydrogenated paraffin
16 feed stocks. It is preferred that the olefin be monounsaturated. It is most preferred that the
17 olefin be an alpha-olefin containing a terminal ethylenic unit.

18
19 Commonly, said olefins would be available in a paraffinic media of the same carbon
20 range. Olefins in the 10 to 14 carbon number range would typically be available from C₁₀ to C₁₄
21 paraffin dehydrogenation in a C₁₀ to C₁₄ paraffin mixture having an olefin content of 5 to
22 20%. Often, the olefin content of said olefin-paraffin mixture would be 8 to 10 weight %.

23
24 The 2-phenyl isomer of the LAB produced in accordance with this invention is of
25 formula:



wherein n is from about 5 to about 17 and preferably from about 7 to about 11.

Process Conditions, Procedures, and Apparatus

The process of this invention can be carried out using the continuous reactive distillation column depicted in FIG. 1. In FIG. 1, a feed mixture of benzene and olefin, generally at a benzene-to-olefin molar ratio range of about 1:1 to 100:1 flows from feed pump 10 to feed inlet 14 via line 12. The feed mixture falls to packed mordenite catalyst bed 32 where alkylation in the presence of the fluorine-containing mordenite occurs. Alternatively, while not depicted in FIG. 1, the benzene and olefin can be introduced separately into the bed with mixing occurring in the bed, or the reactants can be mixed via an in-line mixer prior to introducing the reactants into the catalyst bed, or the reactants can be injected separately above the bed with mixing affected by use of standard packing above the bed, or the reactants can be sparged into the chamber above the bed. The catalyst bed 32 depicted in FIG. 1 for laboratory scale may be made of two lengths of 1.1 inch internal diameter tubing, the lengths being 9.5 inches and 22 inches. In the catalyst bed 32, the falling feed mixture also contacts rising vapors of unreacted benzene which has been heated to reflux in reboiler 42 by heater 40. Such rising vapors pass over thermocouple 38 which monitors temperature to provide feedback to heater 40. The rising vapors of benzene and/or olefin also pass through standard packing 36 (e.g., 7.5 inches of goodloe packing). The rising vapors heat thermocouple 30 which connects to bottoms temperature controller 28 which activates heater 40 when temperature drops below a set level.

Prior to startup, the system may be flushed with nitrogen which enters via line 54 and which flows through line 58. After startup, a nitrogen blanket is maintained over the system. Also prior to startup and during nitrogen flush, it may be desirable to heat catalyst bed 32 so as to drive off water from the fluorine-containing mordenite.

Residual water from the feed mixture or which otherwise enters the system is collected in water trap 24 upon being liquified at condenser 21 (along with benzene vapor). If the feed is very dry (free of water) the water trap 24 may not be needed. Removing water leads to longer

1 catalyst lifetime. Hence, the water trap 24 is optional. The same applies to FIG. 2. Condenser
2 21 is cooled via coolant such as water entering condenser 21 via port 22 and exiting via port 20.
3 As needed, water in water trap 24 may be drained by opening drain valve 26.

4
5 As needed, when LAB content in reboiler 42 rises to a desired level, the bottoms LAB
6 product may be removed from the system via line 47, using either gravity or bottoms pump 48
7 to withdraw the product. When product is so withdrawn, valve 44 is opened.

8
9 In FIG. 1, dip tube 46, which is optional, is employed to slightly increase the pressure in
10 reboiler 42 to thereby raise the boiling point of benzene a degree or two. Likewise, a pressure
11 generator 56 may be optionally employed to raise the pressure of the system. Other standard
12 pressure increasing devices can be employed. Pressure can thus be increased in the system such
13 that the boiling point of benzene increases up to about 200°C.

14
15 In FIG. 1, control mechanisms for heat shutoff 50 and pump shutoff 52 are depicted
16 which serve to shut off heat and pump if the liquids level in the system rises to such levels.
17 These control mechanisms are optional and may be included so that the catalyst bed does not
18 come into contact with the bottoms of the reboiler.

19
20 In the practice of this invention in the alkylation of benzene, a wide variety of process
21 conditions can be employed. In this regard, the temperature in the catalyst bed may vary
22 depending on reactants, rate of introduction into the catalyst bed, size of the bed, and so forth.
23 Generally, the bed is maintained at the reflux temperature of benzene depending on pressure.
24 Typically, the temperature of the catalyst bed is above about 70°C, and most likely about 78°C
25 or more in order to have reasonable reaction rates, and about 200°C or less to avoid degradation
26 of reactants and products and to avoid deactivation of the catalyst by coke build-up. Preferably,
27 the temperature is in the range from about 80°C to about 140°C. The process may be operated
28 at a variety of pressures during the contacting step, with pressures of about atmospheric most
29 typically being employed. When the process is operated using a system as depicted in FIGS. 1
30 and 2, the reboiler temperature is maintained such that benzene and olefin vaporize, the
31 temperature varying depending on olefin, and generally being from about 80°C to about 250°C

1 for olefins having 10 to 14 carbons. The composition of the reboiler will vary over time, but is
2 generally set initially to have a benzene olefin ratio of about 5:1, with this ratio being
3 maintained during the practice of this invention. The rate of introduction of feed into the
4 catalyst bed may vary, and is generally at a liquid hourly space velocity ("LHSV") of about
5 0.05 hr⁻¹ to about 10 hr⁻¹, more typically from about 0.05 hr⁻¹ to about 1 hr⁻¹. The mole ratio of
6 benzene to olefin introduced into the catalyst bed is generally from about 1:1 to about 100:1. In
7 commercial benzene alkylation operations, it is common to run at mole ratios of from about 2:1
8 to about 20:1, which can suitably be employed in the practice of this invention, and to charge
9 said olefins as an olefin-paraffin mixture comprising 5% to 20% olefin content. Said olefin-
10 paraffin mixtures are normally generated commercially through dehydrogenation of the
11 corresponding paraffin starting material over a noble metal catalyst.

12
13 Another continuous reactive distillation apparatus is depicted in FIG. 2. In FIG. 2, the
14 feed mixture enters the reactor via feed inlet 114. The feed mixture falls through the column
15 into catalyst bed 132, wherein alkylation to form LAB occurs. A thermowell 133 monitors the
16 temperature of said catalyst bed 132. The catalyst bed 132 may be optionally heated externally
17 and is contained within 1-1/4 inch stainless steel tubing. Goodloe packing is positioned at
18 packing 136 and 137. LAB product, as well as unreacted benzene and olefin, fall through
19 packing 136 into reboiler 142. In reboiler 142, electric heater 140 heats the contents of reboiler
20 142 such that heated vapors of benzene and olefin rise from the reboiler 142 to at least reach
21 catalyst bed 132. As needed, the bottoms LAB product may be removed from reboiler 142 by
22 opening bottoms valve 144 after passing through line 147 and filter 145. Residual water from
23 the feed mixture, or which otherwise enters the system, may be condensed at condenser 121
24 which is cooled with coolant via inlet line 122 and exit line 120. The condensed water falls to
25 water trap 124, which can be drained as needed by opening drain valve 126. Temperature in the
26 system is monitored via thermocouples 138, 130, and 165. The system includes pressure
27 release valve 166. A nitrogen blanket over the system is maintained by introduction of nitrogen
28 gas via inlet line 154. Level control activator 150 activates bottoms level control valve 151 to
29 open when the liquids level in the reboiler rises to the level control activator 150.

30

While the systems depicted in FIG. 1 and FIG. 2 show single catalyst bed systems, it may be appreciated that multi-catalyst bed reactors are within the scope of this invention, as well as multiple ports for inlet feeds, water traps, product removal lines, and so forth. Moreover, the process may be run in batch mode, or in other continuous processes using plugflow designs, trickle bed designs, and fluidized bed designs.

It is believed that as average molecular weight of olefins increases, particularly when the average number of carbons exceed 14, the selectivity and conversion to LAB, especially LAB with the 2-isomer, may incrementally decrease. If desired, the product of the alkylation using Hf-treated mordenite may be sent to a second, finishing catalyst bed to improve yield. This procedure is optional and is believed to be dependent on the needs and desires of the end user. An example of such a second catalyst is HF-treated clay such as montmorillonite clay having about 0.5% fluoride. Such a catalyst may also serve to lower the bromine number below about 0.1, depending on conditions.

Variable 2-phenyl Isomer Content of Product Using the Mordenite of this Invention In Combination with a Second, Solid LAB Alkylation Catalyst

The fluorine-containing mordenite of this invention generally produces LAB having high 2-phenyl isomer content, such as higher than about 70%. Currently, LAB purchasers who make detergents would prefer to use LAB having a 2-phenyl isomer content in the range from about 30 to about 40 percent. Conventional LAB alkylation technology does not, however, achieve these higher 2-phenyl isomer levels. HF, for instance, produces about 16-18 percent of the 2-phenyl isomer in the product stream from the reactor. Aluminum chloride, on the other hand, produces 26-28 percent of the 2-phenyl isomer in LAB. The present inventor recognized that a need exists for a process which produces a 2-phenyl isomer product in the desired range.

It has now been found that the mordenite of this invention can be used in combination with conventional solid LAB alkylation catalysts, such as silica-alumina (with or without fluorine treatment, such as disclosed in U. S. Patent 5,196,574), clay and aluminum chloride. Since conventional LAB alkylation catalysts produce product having a 2-phenyl isomer content

1 much less than that from the mordenite, combining the mordenite of this invention and a second
2 solid alkylation catalyst may be used to achieve an LAB product having a higher 2-phenyl
3 isomer content than which could be achieved by the conventional, solid LAB alkylation catalyst
4 alone. In practice, the 2-phenyl isomer content of the final LAB product may be varied by
5 adjusting the relative amounts of the two catalysts employed and/or the flow rate of reactants
6 over each catalyst. For a given desired 2-phenyl isomer content of the product, the relative
7 proportions of the two catalysts may vary depending on activity of each catalyst, the type and
8 flow rates of the reactants, temperature, pressure and other process variables.

9
10 FIG. 3 depicts a representative, non-limiting scheme for the practice of this invention.
11 The catalysts, which may be used as a mixture, may be packed in series in the reactor 230 or
12 may be loaded into two reactors aligned in series, are employed in amounts effective to achieve
13 the desired level of 2-phenyl isomer content. If the catalysts are employed in series, whether in
14 the same reactor or in multiple reactors, the amount of the first catalyst in the series is an
15 amount relative to the amount and/or flow rate of the reactants that is insufficient to effect
16 complete conversion of the reactants. The second catalyst may be used in any amount which
17 will complete reaction of the reactants. The fluorine-containing mordenite may be either the
18 first or second catalyst, preferably being in the first bed. Alternatively, reactor 230 may be
19 packed with a mixed bed of the two catalysts.

20
21 The scheme of FIG. 3 is shown in the context of LAB alkylation based on a feed from a
22 paraffin dehydrogenation facility. Thus, in FIG. 3 fresh paraffin is fed to a conventional
23 dehydrogenation apparatus 210 via line 211, with recycled paraffin being introduced from the
24 paraffin column 250 via line 252. Dehydrogenated paraffin from the dehydrogenation apparatus
25 210 is then pumped into an alkylation reactor (or reactors) 230 that contains the fluorine-
26 containing mordenite and a second, solid alkylation catalyst. The dehydrogenated paraffin feed
27 may of course be supplied from any provider. The source of dehydrogenated paraffin (olefin)
28 is not critical to the practice of this invention. LAB product from alkylation unit 230 may
29 thereafter be purified by a series of distillation towers.

30

1 In this regard, alkylation effluent may be delivered to a benzene column 240 by way
2 of line 231. It should be appreciated that the alkylation product may be sent offsite for
3 purification. Further, the particular purification scheme used is not critical to the practice of
4 this invention. The scheme depicted in FIG. 3 is instead representative of a typical
5 commercial operation. In FIG. 3, unreacted benzene is distilled off from the crude LAB
6 product. Benzene is then recycled to the alkylation reactor 230. The benzene-free LAB
7 crude product from the benzene column 240 is pumped through line 241 to paraffin column
8 250 where any paraffin present is distilled off, with the distilled paraffin being recycled to
9 paraffin dehydrogenation unit 210 via line 252. Paraffin-free crude LAB from the paraffin
10 column 250 is transported to a refining column 260 where purified LAB is distilled and
11 removed via line 262. Heavies (e.g., dialkylates and olefin derivatives) are withdrawn from
12 refining column 260 via conduit 261.

13
14 It should be appreciated that columns 240, 250, and 260 may be maintained at
15 conditions (e.g., pressure and temperature) well known to those of skill in the art and may be
16 packed with conventional materials if desired.

17
18 The conventional LAB catalysts used most frequently are HF alkylation catalysts and
19 aluminum chloride alkylation catalysts. Other alkylation catalysts in use today include, various
20 zeolites, alumina-silica, various clays, as well as other catalysts.

21 22 *Representative Examples*

23
24 The following examples are illustrative of the present invention and are not intended to
25 be construed as limiting the scope of the invention or the claims. Unless otherwise indicated, all
26 percentages are by weight. In the examples, all reactants were commercial grades and used as
27 received. The apparatus depicted in FIG. 1 was employed for examples 2-4. The apparatus
28 depicted in FIG. 1 was used for example 5.

29
30 It may be noted that example 2 illustrates LAB production from paraffin dehydrogenate
31 using the fluoride-treated mordenite catalyst of example B, where good catalyst life (250+ hrs)

is achieved without catalyst regeneration, while maintaining a 2-phenyl LAB selectivity of >70% and high LAB productivity without significant loss of fluoride. Comparative example 1, on the other hand, using untreated mordenite, with no fluoride added, shows a rapid decline in LAB production. In addition, examples 3 and 4 illustrate LAB production using a 5:1 molar benzene/C₁₀-C₁₄ olefin feed mix and the fluoride-treated mordenite catalysts of Example B when operating at different LHSV's in the range of 0.2-0.4 hr⁻¹. Catalyst life may exceed 500 hours. Example 5 illustrates LAB production with the fluoride-treated mordenite catalyst where the alkylation is conducted at higher temperatures and under pressure. Examples 6-8 illustrate the performance of three HF-treated mordenite catalysts with different fluoride loadings. Example 9 shows how virtually no alkylation activity is observed with a highly-fluorinated mordenite.

EXAMPLE A

This example illustrates the preparation of a hydrogen fluoride-modified mordenite.

To 30 g of acidified mordenite (LZM-8, SiO₂/Al₂O₃ ratio 17; Na₂O wt% 0.02, surface area 517 m²/g, powder, from Union Carbide Corp.) was added 600 ml of 0.4% hydrofluoric acid solution, at room temperature. After 5 hours the solid zeolite was removed by filtration, washed with distilled water, dried at 120°C overnight, and calcined at 538°C.

EXAMPLE B

The example illustrates the preparation of a hydrogen fluoride-modified mordenite.

To 500 g of acidified, dealuminized, mordenite (CBV-20A from PQ Corp.; SiO₂/Al₂O₃ molar ratio 20; Na₂O, 0.02 wt%; surface area 550 m²/g, 1/16" diameter extrudates, that had been calcined at 538°C, overnight) was added a solution of 33 ml of 48% HF solution in 1633 ml of distilled water, the mix was cooled in ice, stirred on a rotary evaporator overnight, then filtered to recover the extruded solids. The extrudates were further washed with distilled water, dried in vacuo at 100°C, and then calcined at 538°C, overnight.

Analyses of the treated mordenite showed:

F: 1.2%
Acidity: 0.49 meq/g

EXAMPLE 1

This example illustrates the preparation of linear alkylbenzenes using a hydrogen fluoride-modified mordenite catalyst.

To a 500 ml flask, fitted with condenser and Dean Stark Trap was added 100 ml of benzene (reagent grade) plus 10 g of hydrogen fluoride-modified mordenite zeolite, prepared by the method of Example A. The mix was refluxed for 15-20 minutes to remove small amounts of moisture, then a combination of benzene (50 ml) plus 1-dodecene (10 g) was injected into the flask and the solution allowed to reflux for 3 hours.

Upon cooling, the modified mordenite catalyst was removed by filtration, the filtrate liquid flashed to remove unreacted benzene, and the bottoms liquid analyzed by gas chromatography.

Typical analytical data are summarized in Table 1.

TABLE 1

DODECENE CONV. (%)	LAB ISOMER DISTRIBUTION (%)					HEAVIES (%)	LINEAR LAB (LLAB) (%)
	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph		
99.7	79.9	16.6	0.8	1.3	1.3	0.2	95.9

EXAMPLE 2

This example illustrates the preparation of linear alkylbenzenes from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

1 In the example, benzene was alkylated with a sample of C₁₀-C₁₄ paraffin dehydrogenate
2 containing about 8.5% C₁₀-C₁₄ olefins. Alkylation was conducted in a process unit as shown in
3 FIG. 1.

4 Alkylation was conducted by first charging 500 ml of a benzene/paraffin dehydrogenate
5 mix (10:1 molar ratio, benzene/C₁₀-C₁₄ olefin) to the reboiler and 250 cc of the HF-treated
6 mordenite of example B to the 1.1" i.d. reaction zone. The mordenite was held in place using
7 Goodloe packing. The reboiler liquid was then heated to reflux and a benzene plus C₁₀-C₁₄
8 paraffin dehydrogenate mix (10:1 molar ratio, benzene/C₁₀-C₁₄ olefin) continuously introduced
9 into the unit above the catalyst column at the rate of 100 cc/hr. (LHSV=0.4 hr⁻¹).
10

11 Under steady state, reflux. conditions liquid product was continuously withdrawn from
12 the reboiler and water continuously taken off from the water trap. The crude liquid product was
13 periodically analyzed by gas chromatography. The reboiler temperature was typically in the
14 controlled range of 97-122°C. The column head temperature variability was 78-83°C. A
15 summary of the analytical results may be found in Table 2.
16
17
18

After 253 hours on stream, the recovered IIF-treated mordenite catalyst showed by analysis:

F: 1.1%
Acidity: 0.29 meq/g
H₂O: 0.3%

Table 2

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
0	0	1.4		32.3
2	1	3.4		19.7
4	2	5.8	74.9	16.6
6	3	6.6	75.8	25.2
32	4	7.9	80.7	27.0
56	5	7.8	82.7	27.0
69	6	7.3	81.4	27.4
94	7	6.5	82.0	27.8
118	8	6.0	78.4	27.7
142	9	5.9	81.3	26.9
166	10	5.4	81.5	27.3
207	11	5.3	81.3	26.1
229	12	5.1	81.1	27.4
253	13	4.9	81.4	28.1

1 Comparative Example 1

2

3 This example illustrates the preparation of linear alkylbenzenes from paraffin
4 dehydrogenate using an untreated mordenite catalyst.

5

6 Following the procedures of Example 9, the alkylation unit was charged with 250 cc of
7 untreated, calcined, mordenite, (the starting mordenite of Example B), and the liquid feed
8 comprised benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 10:1 molar ratio of
9 benzene/C₁₀-C₁₄ olefin.

10

11 Typical results are summarized in Table 3.

12

13 The recovered mordenite showed by analysis:

14 Acidity: 0.29 meq/g

15 H₂O: 2.1%

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Table 3

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
0	0			11.2
2	1	6.50		9.9
4	2	7.16	73.2	17.1
6	3	7.09	73.1	26.4
22	4	8.61	73.9	26.6
31	5	10.49	67.4	15.8
46	6	7.39	75.0	27.7
70	7	6.39	75.1	28.5
93	8	6.08	73.6	23.0
144	9	5.21	73.6	15.8
157	10	4.40	73.9	26.2
180	11	3.06	69.6	27.1
204	12	1.32		19.5
228	13	1.32		33.3

EXAMPLE 3

This example also illustrates the preparation of linear alkylbenzenes from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

Following the procedures of Example 2, the alkylation unit was charged with 250 cc of the HIF-treated mordenite of Example B, and the liquid feed comprised a benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 5:1 molar ratio of benzene/C₁₀-C₁₄ olefin, the reboiler temperature was typically in the range of 122-188°C, the column head temperature 78-83°C. Typical analytical results are summarized in Table 4.

5

1 After 503 hours on stream, the recovered IIF-treated mordenite catalyst showed on
2 analysis:

10

3 F: 1.0%
4 Acidity: 0.35 meq/g
5 H₂O: 0.1%

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Table 4

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)	Corrected ^a Alkylate Conc. (%)
0	0	1.0		8.9	1.1
2	1	3.5	61.8	0.3	3.5
4	2	7.1	72.1	0	7.1
6	3	6.8	76.7	7.2	7.3
34	4	8.4	79.7	14.3	9.8
71	5	7.2	81.8	14.6	8.5
96	6	6.5	80.8	15.5	7.7
119	7	6.3	80.6	15.1	7.4
643	8	6.0	81.0	14.3	7.0
168	9	5.9	80.7	14.4	6.9
239	10	5.0	78.2	8.8	5.5
263	11	5.3	79.2	13.5	6.2
288	12	5.0	79.6	16.5	6.0
311	13	5.4	79.4	4.1	5.6
335	14	5.5	79.2	8.2	6.0
408	15	4.9	79.4	13.1	5.6
432	16	4.7	78.8	14.4	5.5
456	17	4.4	78.5	14.1	5.1
479	18 ^a	4.7	78.6	2.7 ^b	4.8
488	19 ^b	4.9	78.5	2.4 ^c	5.0
503	20 ^b	5.1	78.9	0.6 ^c	5.1

^a Corrected for benzene in effluent sample.^b Applied pressure 8" H₂O^c Applied pressure 12" H₂O

1 Example 4

2

3 This example also illustrates the preparation of linear alkylbenzenes from paraffin
4 dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

5

6 Following the procedures of Example 2, alkylation was conducted in the glassware unit
7 of FIG. 1 complete with catalyst column, reboiler, condenser and controls. To the reaction zone
8 was charged 500 cc of HF-treated mordenite of Example B. The liquid feed comprised a
9 benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 5:1 molar ratio of benzene /C₁₀-C₁₄ olefin.
10 The feed rate was 100 cc/hr (LHSV:0.2 hr⁻¹).

11

12 Under typical steady state, reflux, conditions, with a reboiler temperature range of 131-
13 205°C and a head temperature of 76-83°C, typical results are summarized in Table 5.

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Table 5

Pressure (Inch H ₂ O)	Reboiler Temp. (°C)	Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)	Corrected* Alkylate Conc. (%)
12	205	2	1	8.2	74.3	0.5	8.3
	193	4	2	9.2	75.0	0.4	9.2
	175	6	3	10.0	74.8	2.3	10.3
	204	21	4	12.7	78.7	0.3	12.7
	146	44	5	11.7	81.0	10.4	12.9
	136	68	6	11.5	81.8	10.0	12.7
		2-3 days	C ^b	11.6	81.4	9.4	12.7
	136	93	7	11.3	82.6	10.8	12.5
		4-5 days	C-1 ^b	11.0	81.8	11.0	12.2
	142	165	8	10.4	83.0	11.4	11.5
	142	189	9	10.2	83.4	10.5	11.2
	146	213	10	9.7	80.2	11.2	10.7
	139	238	11	9.6	83.4	11.1	10.7
	143	261	12	9.9	81.9	11.0	11.0
	133	333	13	9.2	83.4	11.3	10.3
	138	356	14	8.9	83.5	11.1	9.9
	138	381	15	8.8	83.0	11.3	9.8
	131	405	16	8.7	82.8	11.2	9.7

* Corrected for benzene in effluent sample

^b Composite productEXAMPLE 5

This example illustrates the preparation of linear alkylbenzenes from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

Following the procedures of Example 2, alkylation of benzene with C₁₀-C₁₄ paraffin dehydrogenate was conducted using the stainless-steel unit of FIG. 2, complete with catalyst column, reboiler, condenser, and controls. About 250 cc of HF-treated mordenite of Example B

1 was charged to the column. The liquid feed comprised benzene plus C_{10} - C_{14} paraffin
2 dehydrogenate mix in a 10:1 molar ratio of benzene/ C_{10} - C_{14} olefin. The LHSV varied from 0.2
3 to 0.4 hr^{-1} .

4
5 Alkylation was conducted over a range of column and reboiler temperatures and a range
6 of exit pressures. Typical results are summarized in Table 6.

7

8

9

Table 6

Column Temp (°C)	Pressure		Pot Temp. (°C)	Time (hr)	Sample (#)	Alkylate Conc. (%)	2- Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
	DIFF (psi)	EXIT (psi)						
149-129	0.1	0	188	4	1	3.8		6.3
152-126	0	0	200	20	2	1.8		32.7
195-108	0	0	199	25	3	5.7		8.7
218-111	0	0	201	28	4	0.8		67.5
212-118	0	0	201	44	5	8.8	71.7	4.5
209-114	0.2	0	198	52	6	2.4		47.3
228-116	0	0	197	68	7	6.9	72.6	12.4
187-107	0.5	0	197	76	8	2.9	74.6	44.1
				76	9 ^a	4.8	72.9	25.3
					9C ^b	6.8	72.2	1.0
174-107	0	0	178	6	10	4.1	79.2	54.9
170-106	0	0	172	22	11	2.0		59.8
				28	12 ^a	6.6	76.8	26.8
142-107	0	0	136	31	13	4.8	67.9	18.9
141-110	0	0	138	47	14	4.4	65.9	16.9
142-110	0	0	136	55	15	5.0	63.9	16.6
168-111	0	0	131	71	16	4.1	64.8	16.7
170-108	0	0	150	79	17	5.0	72.0	8.8
175-113	0	0	143	95	18	5.9	68.1	15.2
145-106	0	5.2	188	14	19	3.2	60.2	9.0
149-108	0	4.2	186	20	20	4.8	66.3	12.0
160-118	0	11.7	213	29	21	4.2		6.7
160-119	0	9.3	210	44	22	5.2		6.6

^a Composite product^b Stripped composite product

EXAMPLES 6-8

These examples illustrate the preparation of linear alkylbenzenes using hydrogen fluoride-modified mordenite catalysts with different fluoride treatment levels.

Following the procedures of Example 1, the alkylation unit was charged with benzene (100 ml), a 10 g sample of hydrogen fluoride-modified mordenite prepared by the procedure of Example B, plus a mix of benzene (50 ml) and 1-decene (10 g). Three HF-treated mordenites were tested, having the composition:

Catalyst "C" 0.25% HF on mordenite (CBV-20A)

Catalyst "D" 0.50% HF on mordenite (CBV-20A)

Catalyst "E" 1.0% HF on mordenite (CBV-20A)

In each experiment samples of the bottoms liquid fraction were withdrawn at regular periods and subject to gas chromatography analyses. The results are summarized in Table 7.

Table 7

CATALYST	TIME	%LLAB	%ISOS	%HVY	%2Ph	%3Ph	%4Ph	%5Ph	%6&7Ph
D	10	11.75	0.14	0	73.36	21.87	2.89	0.94	1.02
	20	12.43	0.21	0	72.97	21.96	3.14	1.13	0.81
	30	12.88	0.21	0	72.67	22.13	3.03	1.16	1.01
	40	12.27	0.22	0	73.02	21.92	2.85	1.06	1.14
	50	12.15	0.98	0	72.46	21.67	3.21	1.17	1.49
	50	12.24	1.01	0	72.53	21.63	3.23	1.12	1.44
	60	12.28	0.21	0	72.96	22.07	2.93	1.14	0.91
	60	11.98	0.21	0	72.97	22.21	2.93	1.17	0.83
C	10	12.2	0.18	0	72.54	22.46	3.21	0.98	0.82
	20	12.7	0.39	0	71.51	22.61	2.91	1.02	2.13
	30	12.52	0.21	0	71.96	22.68	2.96	1.04	1.36
	40	12.75	0.21	0	71.84	22.57	3.22	1.02	1.25
	50	12.98	0.21	0	71.57	22.81	3.16	1.08	1.39
	60	12.54	0.21	0	71.45	22.81	3.19	1.12	1.44
	60	12.33	0.21	0	71.61	22.87	2.92	1.05	1.31
E	10	10.56	0.05	0	75.19	19.41	2.18	3.22	
	20	12.95	0.15	0	74.36	19.23	3.01	3.4	
	30	13.44	0.18	0	74.11	19.42	3.2	3.27	
	40	13.16	0.15	0	74.16	19.38	3.12	3.34	
	50	13.1	0.15	0	74.43	19.16	3.21	3.28	
	60	12.83	0.15	0	74.28	19.49	2.88	3.35	

CATALYST	TIME	%LLAB	%ISOS	%HVY	%2Ph	%3Ph	%4Ph	%5Ph	%6&7Ph
	60	12.87	0.16	0	73.82	19.97	2.8	3.2	

Example 9

This example illustrates the inactivity of a heavily loaded hydrogen-fluoride modified mordenite catalyst.

Following the procedures of Example 2, the alkylation unit was charged with 100 cc of a hydrogen fluoride-treated mordenite (CBV-20A) prepared by the method of Example B but having a much higher loading of HF (fluoride content 4.8%). The acidity of said HF-treated mordenite was 0.15 meq/g.

No significant amount of alkylated product was detected by gas chromatography.

Claims

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1 What is Claimed is:

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3 1. A process for the production of linear alkylbenzenes, comprising:

4 contacting benzene and an olefin having about 8 to about 30 carbons in the presence
5 of a mixed catalyst bed to form linear alkylbenzenes, wherein the mixed catalyst bed
6 comprises fluorine-containing mordenite and a second, solid linear alkylbenzene alkylation
7 catalyst, wherein the second alkylation catalyst has a selectivity to the 2-phenyl isomer of the
8 linear alkylbenzenes less than the selectivity of the fluorine-containing mordenite.
9

10 2. The process of claim 1, wherein the olefin is obtained by dehydrogenating a paraffin.
11

12 3. The process of claim 1, wherein the linear alkylbenzenes stream is distilled to remove
13 unreacted benzene, unreacted olefin and any components heavier than the linear
14 alkylbenzenes.
15

16 4. The process of claim 1, wherein the fluorine-containing mordenite is made by
17 contacting mordenite with an aqueous hydrogen fluoride composition having a hydrogen
18 fluoride concentration in the range from about 0.1 percent by weight to about 1 percent by
19 weight.
20

21 5. The process of claim 1, wherein the fluorine-containing mordenite has a silica to
22 alumina molar ratio in a range from about 10:1 to about 50:1, wherein the mordenite has been
23 treated by contacting mordenite with an aqueous hydrogen fluoride solution, wherein the
24 hydrogen fluoride in the aqueous solution has a concentration percent by weight.
25

26 6. The process of claim 1 which is operated under conditions effective to produce a 2-
27 phenyl isomer content in the linear alkylbenzenes in the range from about 35 to about 40
28 percent by weight.
29

30 7. The process of claim 1, wherein the benzene and olefin to be contacted with the
31 mordenite has a benzene/olefin ratio of from about 2:1 to about 20:1, wherein the mordenite is

1 maintained at a temperature in the range from about 70 degrees Centigrade to about 200 degrees
2 Centigrade, and wherein the benzene and olefin that contacts the mordenite has a combined
3 liquid hourly space velocity in the range from about 0.05 hr⁻¹ to about 10 hr⁻¹.

4
5 8. The process of claim 1 wherein the fluorine-containing mordenite and the second
6 alkylation catalyst are present in amounts effective to produce linear alkylbenzenes having a 2-
7 phenyl isomer content in the range from about 35 percent to about 40 percent.

8
9 9. The process of claim 1 wherein the second alkylation catalyst is aluminum chloride.

10
11 10. The process of claim 1 wherein the second alkylation catalyst is a fluorine-containing
12 clay.

13
14 11. The process of claim 1 wherein the second alkylation catalyst is a silica-alumina
15 catalyst.

16
17 12. The process of claim 1 wherein the selectivity of the second alkylation catalyst to the 2-
18 phenyl isomer is less than about 35 percent.

19
20 13. Linear alkylbenzenes, which is prepared according to the process of claim 1.

21
22 14. A process for the production of linear alkylbenzenes, comprising:

23 dehydrogenating a paraffin to form an olefin;

24 sending a feed stream of benzene and the olefin through a conduit to a linear
25 alkylbenzenes alkylation reactor containing a fluorine-containing mordenite and a second
26 alkylation catalyst, wherein the second alkylation catalyst has a selectivity to the 2-phenyl
27 isomer of the linear alkylbenzenes less than the selectivity of the fluorine-containing
28 mordenite;

29 reacting the benzene and olefin in the reactor to form a crude linear alkylbenzenes
30 stream;

1 distilling the crude linear alkylbenzenes stream in a first distillation column to
2 separate benzene that did not react and to form a benzene-free linear alkylbenzenes stream;
3 distilling the benzene-free linear alkylbenzenes stream in a second distillation column
4 to separate any paraffin present and to form a paraffin-free linear alkylbenzenes stream;
5 distilling the paraffin-free linear alkylbenzene stream in a third distillation column to
6 provide an overhead of a purified linear alkylbenzene stream and removing a bottoms stream
7 containing heavies.

9 15. The process of claim 14 further comprising recycling the unreacted benzene from
10 distillation of the crude linear alkylbenzenes stream to the conduit.

12 16. The process of claim 14 further comprising recycling the paraffin to the
13 dehydrogenating step.

15 17. The process of claim 14 further comprising dewatering the portion of the primary feed
16 stream prior to contact with the fluorine-containing mordenite.

18 18. The process of claim 14 wherein the second alkylation catalyst is a silica-alumina
19 catalyst.

21 19. The process of claim 14 wherein the second alkylation catalyst is aluminum chloride.

24 20. The process of claim 14 wherein the second alkylation catalyst is fluorine-containing
25 clay.

27 21. The process of claim 14 wherein the fluorine-containing mordenite is made by
28 contacting mordenite with an aqueous hydrogen fluoride composition having a hydrogen
29 fluoride concentration in the range from about 0.1 percent by weight to about 1 percent by
30 weight.

31

5

1 22. The process of claim 14 wherein the mordenite and the second catalyst are present as
2 a mixed bed in the reactor.

3

10

4 23. The process of claim 14 wherein the mordenite and the second catalyst are packed in
5 the reactor in series.

6

15

7 24. The process of claim 23 wherein the feed stream first contacts the mordenite.

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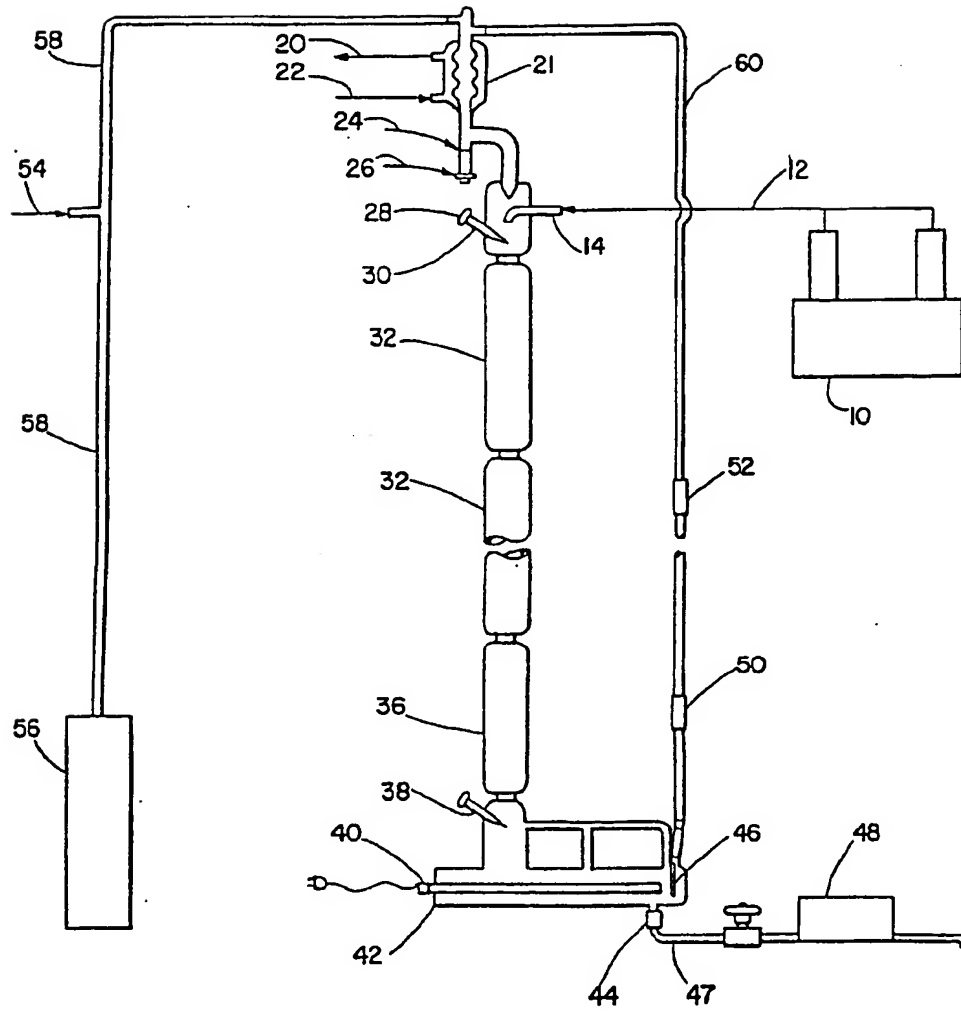
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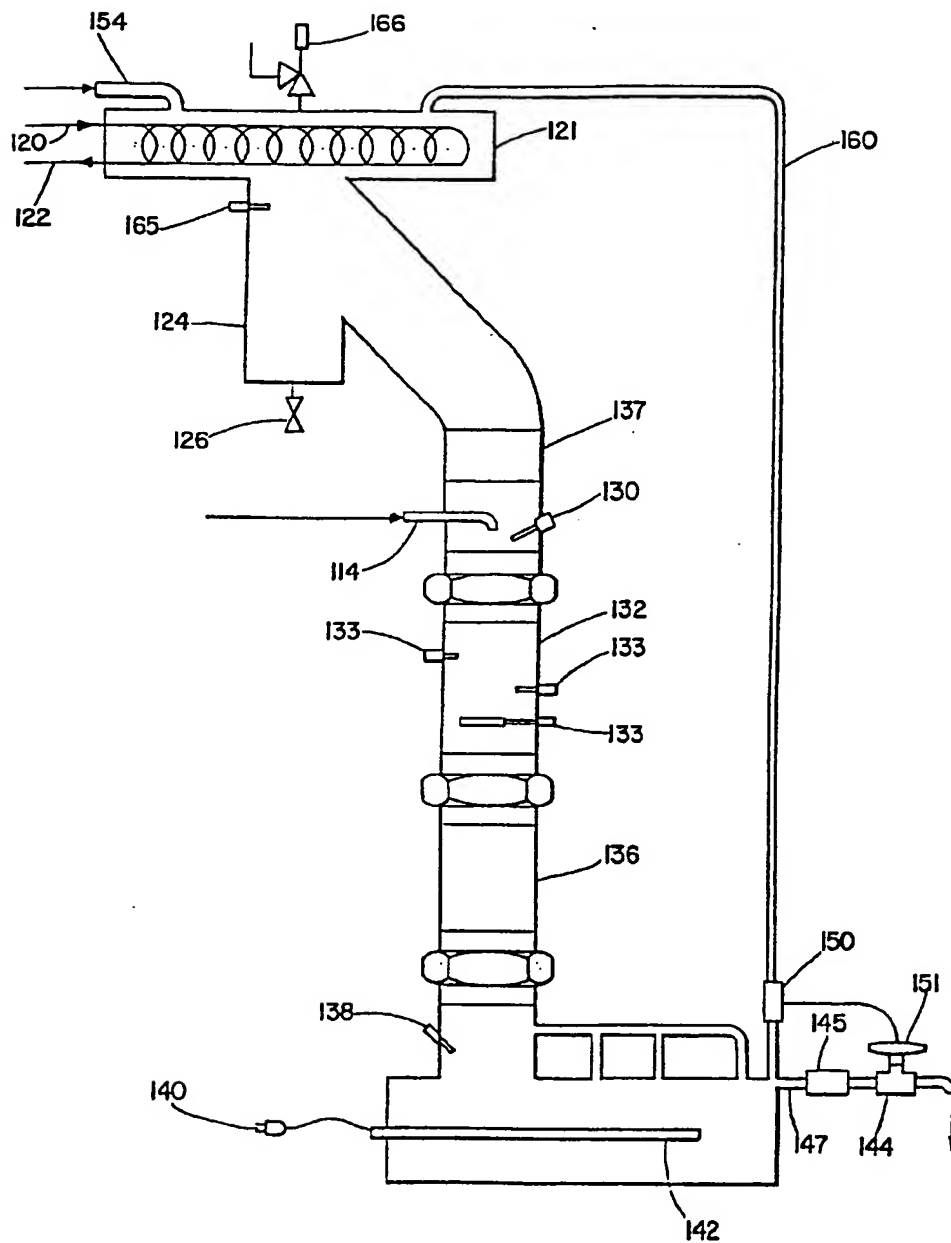
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*Fig. 1*

*Fig. 2*

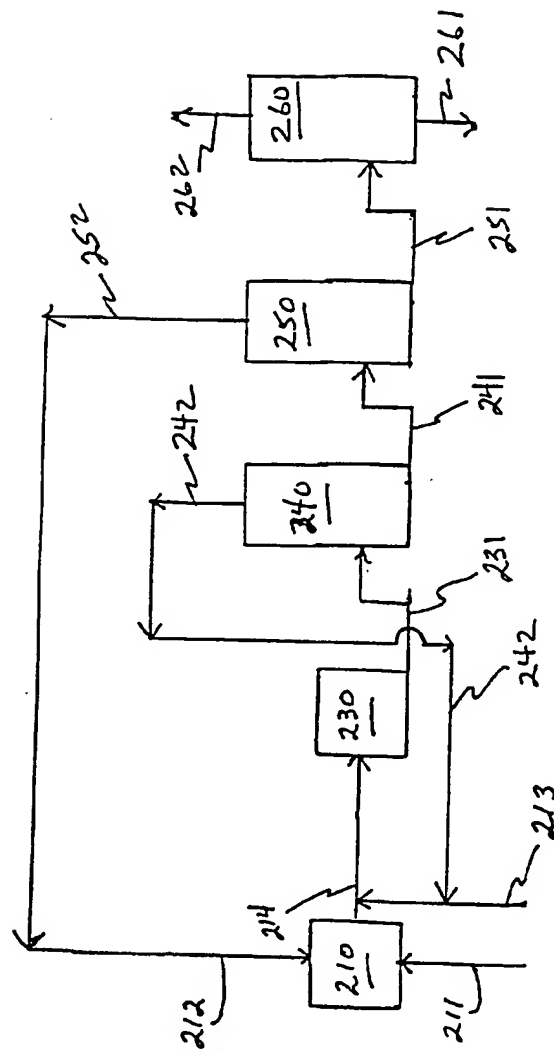


FIG. 3

INTERNATIONAL SEARCH REPORT

Int. and Application No
PCT/US 99/24275

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07C15/107 C07C2/66 B01J29/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 29063 A (HUNTSMAN PETROCHEMICAL CORPORATION) 14 August 1997 (1997-08-14) claims	1-24
A	EP 0 160 145 A (EXXON RESEARCH AND ENGINEERING COMPANY) 6 November 1985 (1985-11-06) claims	9
A	EP 0 589 511 A (ENICHEM AUGUSTA) 30 March 1994 (1994-03-30) claims	11
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the International filing date but later than the priority date claimed "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
Date of the actual completion of the International search 8 March 2000		Date of mailing of the International search report 16/03/2000
Name and mailing address of the ISA European Patent Office, P.O. 5818 Patentstein 2 NL - 2200 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 001 epo nl, Fax (+31-70) 340-5018		Authorized officer Van Geyt, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9729063 A	14-08-1997	US 5847254 A	08-12-1998
		CA 2244834 A	14-08-1997
		CN 1210509 A	10-03-1999
		EP 0882003 A	09-12-1998
		US 5777187 A	07-07-1998
EP 0160145 A	06-11-1985	JP 60228435 A	13-11-1985
EP 0589511 A	30-03-1994	IT 1255512 B	09-11-1995
		AT 160560 T	15-12-1997
		BG 61806 B	30-06-1998
		BG 98121 A	15-11-1994
		CA 2106621 A	25-03-1994
		DE 69315403 D	08-01-1998
		DE 69315403 T	09-04-1998
		DK 589511 T	04-05-1998
		ES 2109424 T	16-01-1998
		GR 3025535 T	27-02-1998
		PL 300466 A	18-04-1994
		RO 111360 A	30-09-1996
		RO 111455 A	31-10-1996
		US 5574198 A	12-11-1996



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(21) International Application Number: PCT/US99/24275 (22) International Filing Date: 19 October 1999 (19.10.1999) (30) Priority Data: 09/174,891 19 October 1998 (19.10.1998) US (60) Parent Application or Grant HUNTSMAN PETROCHEMICAL CORPORATION [?]; (). ANANTANENI, Prakasa, Rao [?]; (). O'KEEFE, Robert, M.; ().	Published			
(54) Title: ALKYLATION OF BENZENE TO FORM LINEAR ALKYL BENZENES USING FLUORINE-CONTAINING MORDENITES (54) Titre: ALKYLATION DU BENZENE POUR LA FABRICATION D'ALKYL BENZENES LINEAIRES AVEC UTILISATION DE MORDENITES FLUOREES				
(57) Abstract <p>This invention is directed to a fluorine-containing mordenite catalyst and use thereof in the manufacture of linear alkylbenzene (LAB) by alkylation of benzene with an olefin. The olefin may have from about 10 to 14 carbons. The fluorine-containing mordenite is prepared typically by treatment with an aqueous hydrogen fluoride solution. The benzene alkylation may be conducted using reactive distillation. This invention is also directed to a process for production of LAB having a high 2-phenyl isomer content by use of the fluorine-containing mordenite in conjunction with a conventional solid LAB alkylation catalyst. The two catalysts may be used in a mixed catalyst bed or may be packed in series, with the relative proportions being adjusted to provide a desired 2-phenyl isomer content in the final product.</p>				
(57) Abrégé <p>La présente invention concerne un catalyseur à mordenite renfermant du fluor et son emploi dans la fabrication d'alkylbenzènes linéaires (LAB) par alkylation du benzène avec une paraffine. Cette paraffine peut comporter de 10 à 14 atomes de carbone. La mordenite fluorée s'obtient généralement par traitement avec une solution aqueuse de fluorure d'hydrogène. L'alkylation du benzène peut se faire par distillation avec réaction. Cette invention concerne également la production de LAB à teneur élevée en 2-phényle isomère au moyen d'une mordenite fluorée avec un catalyseur d'alkylation LAB solide classique. Les deux catalyseurs peuvent être utilisés dans un lit catalytique mélangé ou bien être empilés en série, avec ajustement des proportions relatives en vue de l'obtention de la teneur requise en 2-phényle isomère pour le produit final.</p>				



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(54) Title: ALKYLATION OF BENZENE TO FORM LINEAR ALKYL BENZENES USING FLUORINE-CONTAINING MORDENITES (54) Titre: ALKYLATION DU BENZENE POUR LA FABRICATION D'ALKYL BENZENES LINEAIRES AVEC UTILISATION DE MORDENITES FLUOREES		
(57) Abstract <p>This invention is directed to a fluorine-containing mordenite catalyst and use thereof in the manufacture of linear alkylbenzene (LAB) by alkylation of benzene with a paraffin. The paraffin may have from about 10 to 14 carbons. The fluorine-containing mordenite is prepared typically by treatment with an aqueous hydrogen fluoride solution. The benzene alkylation may be conducted using reactive distillation. This invention is also directed to a process for production of LAB having a high 2-phenyl isomer content by combining LAB product from the fluorine-containing mordenite product from a conventional LAB alkylation catalyst such as hydrogen fluoride.</p> (57) Abrégé <p>La présente invention concerne un catalyseur à mordenite renfermant du fluor et son emploi dans la fabrication d'alkylbenzènes linéaires (LAB) par alkylation du benzène avec une paraffine. Cette paraffine peut comporter de 10 à 14 atomes de carbone. La mordenite fluorée s'obtient généralement par traitement avec une solution aqueuse de fluorure d'hydrogène. L'alkylation du benzène peut s'effectuer par distillation avec réaction. Cette invention concerne également un procédé de fabrication de LAB à forte teneur en 2-phényl isomère qui consiste à combiner une substance LAB tirée d'un produit mordenite fluoré et un catalyseur d'alkylation LAB classique tel qu'un fluorure d'hydrogène.</p>		